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The main thrust of this research continues in the same vein: to design, fabricate, and characterize novel optical fibers of relevance to the general phototonics mission of the Air Force. This includes, but is not limited to, fiber lasers, fiber devices (active and passive), and novel concepts for fiber sensors. Work is in progress on optical fiber sensors for gas detection of fire suppressants, the fabrication of optical planar waveguides, the development of a new technique for the measurement of thin films, and a novel high-temperature optical fiber sensor.

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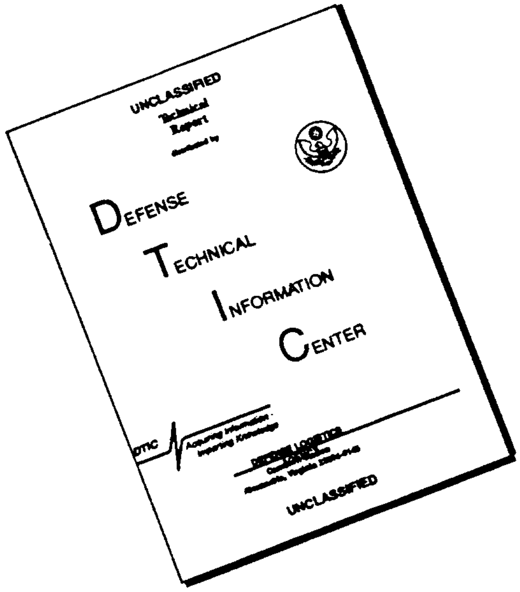


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# Final Report

to the Air Force Office of Scientific Research: Physics

F49620-93-1-0049

Research Support for the Laboratory for Lightwave Technology

Division of Engineering, Brown University

Providence, RI 02912

January 1, 1993-December 31, 1995

T.F. Morse, Professor of Engineering

## 1. Objectives

The main thrust of this research continues in the same vein: to design, fabricate, and characterize novel optical fibers of relevance to the general photonics mission of the Air Force. This includes, but is not limited to, fiber lasers, fiber devices (active and passive), and novel concepts for fiber sensors. Work is in progress on optical fiber sensors for gas detection of fire suppressants, the fabrication of optical planar waveguides, the development of a new technique for the measurement of thin films, and a novel high-temperature optical fiber sensor.

## 2. Status of Effort

The Laboratory for Lightwave Technology at Brown University is one of the two university laboratories in the US at which it is possible to design, fabricate, and characterize optical fiber preforms and optical fibers. At the heart of this research is a novel aerosol process that is able to place low pressure precursors in a convective stream and transport them into a reaction zone. This process is also being used a program to make novel glass compositions for optical planar waveguides on a Si substrate, as well as to develop fiber lasers for a host of new sensors. Further details of the results accomplished in 1993 and 1994 are contained in the status reports for those years, respectively.

## 3. Accomplishments/New Findings

There are several areas of research that have proved to be of significance over the past year. Perhaps the most important of these is the development of a novel optical fiber sensor capable of monitoring in-situ thin film growth in real time. We are currently looking into the possibility of obtaining a patent for this concept/device/ The principle is quite simple, light (either a laser diode or white light) is sent into an optical fiber whose end is placed in a deposition region. This can be used in sputtering, MOCVD, CVD, and MBE. It is of particular importance in MOCVD, where in-situ measurements are, at best, either non-existent, or extremely difficult. This is due to the deposited material also fogging any optical window used to bring a light signal in and out of the chamber. The deposition on the end of the optical fiber mimics the deposition on an appropriate substrate. Light is sent into the fiber, and, as the film grows on the end of the fiber, it functions as a Fabry-Perot of changing length. Thus, interference fringes can be clearly monitored, and each quarter wavelength of the intensity corresponds to a $\lambda/4n$ deposition thickness, where n is the refractive index. To eliminate noise and variation in the signal laser, standard signal processing techniques have been employed. From the experimental measurements, and from modeling the procedure, it is possible to obtain the refractive index, a Gaussian scattering coefficient, and the thickness, all as a function of time. In essence, this is a reflectance measurement that is analogous to ellipsometry at 90 degrees. For this reason, as can be seen from the Fresnel equations, the results are independent of polarization. This type of in-situ measurement provides, with a high degree of experimental simplicity, information that can only be obtained with expensive, difficulty to use techniques.

The above considerations are pertinent to single layer films. If multi-layer stacks are deposited, as is the case for laser mirrors, the following diagnostic technique can be employed. We consider an application of the above technique to a stack of 1/4 wave plates for laser mirrors, for example. If we monitor wavelength vs. intensity for the real time evaluation of the changing reflectivity of such a stack, then we can know exactly when we have reached the desired value of the reflectivity. This is of importance in making mirrors on the ends of small laser diodes, where bulk optical measurements can not be reasonable made. We have applied this experimental and analytical concept to a stack of $Si_3N_4$, and $SiN_x$. Agreement between theory and experiment are excellent. A further consequence of such a film at the end of the fiber is as follows. The $Si_3N_4$, and $SiN_x$. are quite refractory, and the oscillations in optical density form what is the analog of a Bragg grating at the end of the fiber. It is known that if a Bragg grating is subject to temperature or strain, the wavelength value that exhibits maximum reflectivity changes as a function of temperature. Bragg gratings have the disadvantage that for temperatures over 500 centigrade, the grating "washes out". We have demonstrated that a reflective stack of $Si_3N_4$, and $SiN_x$. can be used to sense temperature at over 1000 centigrade.

The above concepts are in the process of being patented, and, for this reason, we have not published our results. The commercial applications would be in several areas. First, there are no reasonably inexpensive, convenient in-situ monitoring devices for MOCVD, the process by which most of the chips in the world are made. Only the quartz oscillator is in common use, and this merely measures the deposition on the oscillator "pendulum". Our technique provides not only thickness measurements, but information on the variation of refractive index and surface roughness as a function of time. These results can be obtained in nearly "real time", so that feed-back can be used to control the stoichiometry and integrity of the film. In conjunction with a small firm, ION OPTICS, we hope to patent and commercialize this novel film thickness monitor.

We had mentioned above that this concept, utilizing a white light source can also function as an indicator for the in-situ measurement of film reflectivity as the 1/4 wave stacks are grown. An additional plus of this concept is the following. With a grown stack of silicon nitride layers, if they are heated, the thermal expansion causes the stack to expand, and the peak reflectivity shifts as a function of temperature. We have shown this to be linear over more than 1,000 centigrade. This could be a commercially viable optical fiber sensor in that the films could be grown on thousands of fiber simultaneously, while using only one fiber to monitor the desired reflectivity. This could provide an inexpensive temperature monitor for aircraft, ship, or aircraft engine temperature monitoring. We are pursuing this.

A second concept that was developed and for which we are seeking a patent is the following. It has long been known that the presence of an absorber within a laser cavity spoils the gain. By introducing an absorber within the cavity of an erbium fiber laser, we have been able to detect the presence of acetylene. This can be applied to any absorber that has an absorption signature under the gain bandwidth of the fiber laser. We were able to tune the device over 18 nm by gluing the Bragg grating to a thin strip of plastic, and then bending the plastic with the fiber on the concave side. By shifting the wavelength .12 nm, with acetylene within a gas cell within the fiber laser cavity, a change of intensity of 50 dB was recorded. This allows the possibility of spectroscopy at a distance, with the sensor itself the size of a fountain pen. The Air Force is interested in monitoring the presence of Halon replacements for putting out aircraft engine fires. In the commissioning of new engines, it is necessary for the fire suppressant system to pass a rigorous test with regard to delivery of the new, non ozone damaging, flame retardants. All of these have absorption signatures under the gain bandwidth of a Tm, or Tm-Ho fiber laser, so the concept of FLICS could be used for such detection. Present detectors have rise times in excess of 100 ms, and the intra-cavity concept considered her, would have a rise time of the order of several microseconds.

We had reported on HOCC's in the past. These are Highly OverCoupled Couplers. Instead of stopping the fabrication of a fused taper coupler after several cycles, we continue and pull these couplers for hundreds and even thousands of cycles. The sensitivity to length, and temperature causes the splitting ratio to change. Placing such a device within an erbium ring laser has allowed us to temperature tune the output of the erbium fiber by over 20 nm, with a temperature change of 5 degrees centigrade. We believe that by placing an absorption cell within the cavity, we will be able to obtain a temperature tuned spectrometer, and work is in progress on this concept.

## 4. Personnel

### Faculty
T.F. Morse 1 month (university supported)
W. Risen 1/2 month

### Technical Staff
L. Reinhart (research engineer) 10.5 months

### Graduate students
Yifei He, 1/3 academic year
Juan Hernandez-Cordero 1/2 month summer
Padma Rajagopalan, academic year, 2 months summer
Eric Wetjen, 2 months summer, 1/2 academic year
Roman Schubochkin, 2 months summer, 1/2 academic year

## 5. Publications: 1995
1. Q. Zhang, D.A. Brown, L. Reinhart, and T.F. Morse, "Linearly and nonlinearly chirped Bragg grating filters fabricated on curved fibers", Optics Letters, vol. 20, p. 1122, 1995.
2. T.F. Morse, Kyungwhan Oh, and L. Reinhart, ", Carbon Dioxide Detection using a Co-Doped Tm-Ho Optical Fiber", European Symnposium on Optics for Environmental and Public Safety, 19-23 June, 1995, Munich Germany, SPIE Publication.
3. H.-C. Chang, T.F. Morse, and B. Sheldon, "Infiltration time During Isothermal Chemical Vapor Infiltration", J.Am. Ceram. Soc., to appear.
4. Q. Zhang, H. Kung, J.E. Townsend, J.E. Chen, L. Reinhart, and T.F. Mors, "The Use of highly overcoupled couplers to detect Bragg wavelength shifts in strain measurements", Electronics Letters, vol. 31, p. 480, 1995.
5. Yifei He. B. Sheldon, and T.F. Morse, "Optical fiber technique for monitoring the growth of a silicon nitride thin film", submitted for publication.
6. A. Kilian C.H. Wei, and T.F. Morse, "a
Aerosol Synthesis of nanoscale ceramic oxides", submitted for publication.

## 6. Interactions/Transitions
### a. Presentations at Meetings, invited Lectures
1. April 1995. AT&T Bell Laboratories, Murray Hill, NJ, New Techniques for Optical Planar Waveguides
2. April 1995, Ceramics Department, Rutgers University, New Concepts in Optical Fiber Sensors

3. May 1995, Department of Civil Engineering, university of Conn., Optical Fiber Sensors in Civil and Environmental Engineering
4. June 1995, Ruhr University Bochum, Germany, Novel Concepts in Optical Fiber Gas Detection.
5. June 1995, European Symnposium on Optics for Environmental and Public Safety, Munich, Germany, A new technique for carbon-dioxide detection.
6. November, 1995. Aerosol Processing Techniques for Glass and Ceramic Materials, National Meeting, American Ceramic Society, Glass and Optical Materials Division.

**b. Consultation with Other Laboratories**

1. Photonics Laboratory, James Battiatio, Griffiss Air Force Base, New York. Cooperative program on co-doped optical fiber lasers.
2. Ion Optics, Bedford, MA. Dr. E. Johnson. Development of technique and commercialization of instrument for thin film monitoring.
3. AT&T Bell Laboratories (Now Lucent Technologies). Dr. John MacChesney and Dr. A. Kilian, optical planar waveguides using novel glass compositions. Dr. D. Digiovanni, novel fibers and lasers. Lucent Technologies (Atlanta), we are trying to see of our technique for planar waveguides can be used for the top cladding layer of flame hydrolysis deposited substrates, Dr. L. Cohen. Lucent Technologies (Whippany, NJ), Dr. J. Simpson on fiber lasers and devices. We co-chaired a National Optical Materials meeting under the aegis of the MRS in San Fransicso last month.
4. Physical Optics Corporation, Torrance, CA . Dr. Robert Lieberman
5. The Litton Corporation, Dr. John Anderson, Mountain View, CA.
6. The Ben Franklin Institute, Pittsburgh, CA. T. F. Morse is a member of the original board of NEOMT, National Electro-Optics Manufacturing Technology. We have submitted a proposal with the Litton Corporation to the Man-Tech program, and it is expected that funding will be forthcoming in the near future.
7. At ATMI (Advanced Technology Materials, Inc.), we are cooperating with Dr. Joan Redwing and Dr. M. Tischler to use our thin film monitoring technique to examine the growth of GaN. This is perhaps the most important new material, now that Nakamura has demonstrated electric excitation of blue laser light. Little is understood about this material, and we will be able to measure refractive index, and growth at high temperatures. Dr. Redwing is in the process of modifying their GaN reactor to accommodate our fiber sensor.
8. The Polaroid Corporation, Dr. Hong Po. We have been engaged in a joint project from NASA to make Tm doped fiber in which we can write gratings at 785 nm. Also, at the Polaroid Corporation, Dr. J. Chen will

modify his deposition system for laser mirrors so that we can determine if our thin film technique that has been applied to silicon nitride is equally applicable to other systems.
9. Thiokol International. Dr. J. Goela, consultation in the development of new techniques for CVD of ceramic materials.
10. West Point Military Academy, Dr. R. Sadowski, cooperative efforts in specialty fibers for photonic switching.

## 7. Dissertations Completed in 1995

a. Yifei He, Optical Fiber Monitoring of Thin Film Deposition, Ph.D.
b. Juan Hernandez-Cordero, Development of a Gas Sensor Based on Fiber Laser Intracavity Spectroscopy (FLICS), M.Sc.

## 8. Patents

1. A patent with AT&T (now Lucent Technologies) is being submitted on an aerosol technique for optical planar waveguides.
2. A patent on fiber laser intra-cavity spectroscopy has been submitted to the US patent office.
3. A patent in progress on the fiber optical technique for in-situ measurement of thin film deposition.
4. As an addendum to the above patent, the use of a refractive layered stack of silicon nitride on the end of an optical fiber for a high temperature fiber sensor.

## 9. Future Work

One particular modification of intra-cavity spectroscopy that we wish to pursue is described as follows. If light is sent into a crystal so that there is total internal reflection and there are many reflections, then if a substance is placed on the outside of the crystal, absorption will occur through the evanescent wave. This is the basis of ATR (Attenuated Total Reflection) spectroscopy. We will modify this concept through the following experiment. The output coupler of a Coherent 506 dye laser will be replaced with a coated aspheric lens that focuses the light into an optical fiber. The fiber, with length of the order of a few meters will be gold coated at the end to produce a highly reflective output coupler. The dye laser cavity will now be defined by the rear plane mirror and the gold coated fiber end. If a taper is pulled in the fiber, then we will have established an ATR cell within the laser cavity. Higher sensitivity in the range of tunability of the laser should result as a consequence of two factors. First, the interaction of the light through the evanescent wave will be continuous along the fiber, and will produce a much greater interaction than a typical ATR cell. Second, by virtue of the fact that the cell is intra-cavity, an enhancement of sensitivity of at least several orders of magnitude will occur. The experiment to be performed will be to place a few drops of Rhodamine 6G in solution, place the evanescent wave section of the fiber in the solution, and then tune the laser through the absorption wavelength region to test for minimum sensitivity. This is a model experiment for the situation in which the thin evanescent wave section is coated with a "getter" molecule that has an affinity for a specific protein or biological molecule. We believe that there are numerous biological applications and implications for such an experiment, should it prove successful. In addition, we plan to continue work on the projects cited and hope that there will be a possible commercialization of some of these concepts in the not too distant future.

## 10. Research Support from Other Sources

Although research has been going extremely well, funding has not matched our expectations. The other funding at the present time is a subgrant from MIT through an INEL program for monitoring of crack growth in concrete structures. We believe that we have conceptually solved the problem of compatibility of optical fibers embedded in concrete by the following trick. Instead of embedding the fiber in the concrete, the fiber is placed in a very thin sheet of polyester film. This film can be retrofitted to existing concrete structures. The fiber is curved in the film, making a snake like path. When a crack in the concrete appears, it propagates through the film. If the crack is at an angle to the fiber (and with two fibers this can be guaranteed), then microbending occurs at the crack. This causes a loss in transmitted light, which can be continuously monitored with an inexpensive detector and diode. If the light loss exceeds some value, an alarm is activated, and the location of the crack can be then detected with a portable (and more expensive) OTDR.

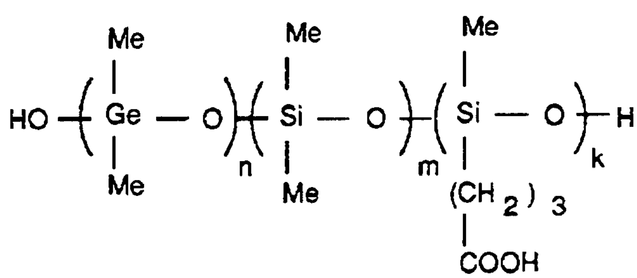
## 11. Pending Proposals

1. A GOALI proposal to NSF with ATMI as the industrial host.
2. STTR submitted to DOD with ION Optics as industrial partner. (Thin film growth)
3. STTR submitted to DOD with ATMI as the industrial host. (In-situ Monitoring of GaN.)

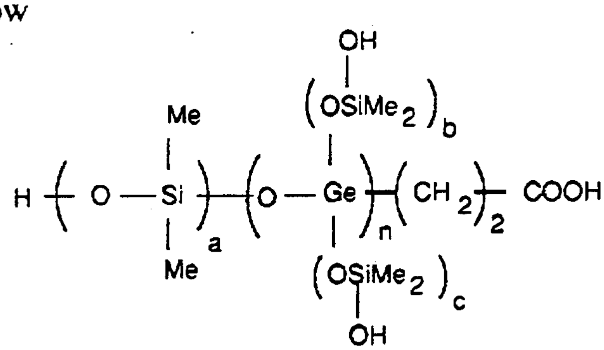
## 12. Additional Research Effort of Prof. W. Risen, Jr., Department of Chemistry

Considerable progress was achieved in 1995 along our chemical approaches to developing new optical materials and new glass structures. These approaches are designed to lead to: (a) $SiO_2$ and similar films for Si, $SiO_2$, $Al_2O_3$ and other substrates produced at relatively low temperature; (b) novel structures with compositionally controlled, higher index oxide materials based on new Ge and Si containing precursors; (c) lanthanide silicate thin films and patterned waveguide structures; (d) patterned $SiO_2$ and $Si_xGe_{1-x}O_2$ planar waveguide structures formed using UV patterning sources;(e) transition metal silicate and germanosilicate thin films; and (f) adhesion structures formed at interfaces of optical fibers and other structures, such as V-grooves in Si planar waveguide substrates.

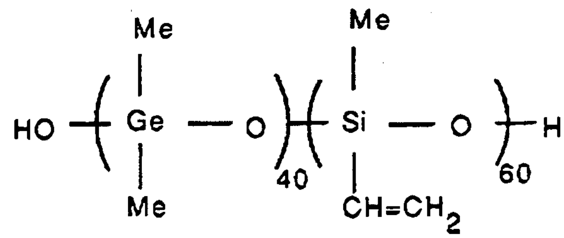
Particularly noteworthy is the achievement of several new classes of germanosiloxane polymeric materials and their successful conversion to $Si_xGe_{1-x}O_2$ glasses. The synthesis of such material precursors should give rise to a number of possible glassy materials containing metal ions and clusters in high refractive index waveguides as well as the germanosilica compositions. These syntheses therefore have been included in the patent filing done in December 1995. The syntheses include one leading to carboxypolygermanosiloxane (CPGS), the composition of which is represented stoichiometrically, but not necessarily in terms of monomer sequence, by:



The syntheses we have achieved also include a germanium sesquioxide siloxane copolymer (GSOSC), which is believed to be represented by the general formula shown below



In addition, we carried out syntheses to afford such precursor polymers as the following vinyl containing polygermanosiloxane (VPGS), and related linear copolymers.




These compositions are in addition to the germanyl esters of carboxylated polysiloxanes reported in last year's report. Thus, the compositional and molecular type range has been extended greatly. All of these compositions are of considerable interest, but the chemistries of Ge and Si containing compounds are so different, especially with respect to hydrolysis, that new and rather unusual multiphase syntheses have had to be designed to achieve them.

We have employed these and the carboxylated polysiloxane precursor molecules to make several useful types of structures. First, they have been used to adhere optical fibers to Si v-grooves with resultant interfacial layers of several refractive indices. Second, they have been used to make microlenses. These microlenses are protrusions on silica, borosilicate and othe substrates and have shapes that give them relatively long focal lengths. In addition, we have used the photocrosslinking of the new carboxysiloxanes followed by ion exchange to make lanthanide silicate microlenses. Third, we have made films of both the lanthanide containing glasses and the related lanthanide ionomers on fibers. The study of their optical properties is underway.

Throughout this period, we have continued to develop the discoveries. This lead to a provisional patent application filed in December, 1995. The material in that form is now being drafted in the form of four separate patents, tentatively titled: (a)Silica, Silicate and Germanosilicate and Glass Films and Patterned Glass Structures, Including those Comprising Lanthanide and Other Metal Ion Compositions; (b) Germanosiloxane Materials and Glass Optical Components Made From Them; (c) Attachments of Waveguide Structures and of Silicon, Germanium and Oxide Glasses Comprising Them; and (d) Microlens Formation.

In the related work on lanthanide ionomers, wehave made several interesting discoveries. One is that the clustering of lanthanide ions in organic ionomers we synthesized leads to novel fluorescence into the 1.5 micron region for Er(III) and Er(III)/Yb(III) materials from 800nm and 980nm, respectively,as well as strong fluorescence in the near infrared for Sm(III) and Dy(III) from 1064nm excitation. It is interesting that the analogous lanthanide carboxypolysiloxanes appear to behave very differently. The initial observations have been described (Dec. 1995 ACS Meeting) and recently published (J. Polymer Sci. B. Polymer Physics 34, 151 (1996), and their morphology has been reported (Polym Pre.37,1 (1996)). However, the work continues on these materials because of their potential for upconversion and because of the great differences between the behavior of related ionomers.